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Stable Alkylvanadium(V) Compounds Containing Bulky Imido and Amido Ligands

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Summary: Treatment of $t\text{-Bu}_3\text{SiNHLi}$ with an equimolar amount of VOCl_3 yields $(t\text{-Bu}_3\text{SiN})(t\text{-Bu}_3\text{SiNH})\text{VCl}_2$ (**1**), which on treatment with PCl_5 gives $(t\text{-Bu}_3\text{SiN})\text{VCl}_3$ (**2**). Alkylation of **1** with MgMe_2(dioxane), $\text{Mg}(\text{CH}_2\text{-}t\text{-Bu})_2$, or $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ yields crystalline (**3a,b**) or waxy (**3c**) complexes $(t\text{-Bu}_3\text{SiN})(t\text{-Bu}_3\text{SiNH})\text{VR(Cl)}$ (R = Me (**3a**), $\text{CH}_2\text{-}t\text{-Bu}$ (**3b**), CH_2SiMe_3 (**3c**)), which show pronounced thermal stability. Use of excess LiMe results in the first structurally characterized alkylvanadium(V) complex, $\text{Li}[(t\text{-Bu}_3\text{SiN})_2\text{VMe}_2]$ (**4**), containing a ligand-shielded solvent-free lithium ion, which is coordinated only to the two imido nitrogen atoms.

Complexes of d^0 transition metals and f elements with hydrocarbyl ligands are known to promote olefin polymerization[1] and C–H activation[2] reactions. The limited development of such chemistry for first-row transition metals beyond group 4 is related to the low stability of the d^0 oxidation state of these metals. Very few thermally stable alkylvanadium(V) complexes have been isolated.[3] The reduction of vanadium(V) precursors to lower oxidation state species on attempted alkylation[4] has been countered, with partial success, by incorporation of good electron-donating imido ligands.[3,5] Wolczanski has made extensive use of sterically bulky ligands such as $t\text{-Bu}_3\text{SiO}^-$ (silox)[6] to stabilize electron-deficient early-transition-metal complexes. Here we report that the use of the bulky imido and amido analogues[7] of silox results in thermally stable crystalline alkylvanadium(V) complexes, including the first structurally characterized member of this series.

Treatment of VOCl_3 with $t\text{-Bu}_3\text{SiNHLi}$[8] led to the new yellow crystalline complex **1**[9,10] (eq 1), containing an amido and an imido ligand, in over 60% yield (based on the lithium salt) together with $t\text{-Bu}_3\text{SiNH}_3\text{Cl}$ and unidentified vanadium compounds, presumably oxyhalide species.

$$\text{VOCl}_3 + t\text{-Bu}_3\text{SiNHLi} \xrightarrow[-20\,^\circ\text{C}]{\text{toluene}} \underset{1}{(t\text{-Bu}_3\text{SiN})(t\text{-Bu}_3\text{SiNH})\text{VCl}_2} \tag{1}$$

This unusual *one-step* synthesis is very sensitive to the reaction conditions; VOCl_3 must be added to a solution of the lithium salt (and not the converse) and the reaction temperature carefully controlled. Attempts to improve the yield by varying the conditions or by using more than 1 equiv of $t\text{-Bu}_3\text{SiNHLi}$ led only to reduction of vanadium. Complex **1** has been characterized by ^{1}H, ^{13}C, and ^{51}V NMR and IR spectroscopy, mass spectrometry, and elemental analysis, as have all other complexes synthesized (unless otherwise mentioned). Although the observation of the parent molecular ion peak (M; m/e = 548) in the mass spectrum does not exclude the possibility of the complex existing as a labile dimer, the steric crowding at the required five-coordinate vanadium appears to rule out such a structure.

The amido ligand in **1** was removed with use of excess of PCl_5 in toluene at 50 °C to give red crystals of $(t\text{-Bu}_3\text{SiN})\text{VCl}_3$ (**2**)[11] in high yield. An alternative synthesis of **2** was attempted by reaction of VOCl_3 with $t\text{-Bu}_3\text{SiNCO}$,[12] in analogy with established routes to (phenylimido)vanadium complexes.[3,13] However, this led only to unreacted starting materials. Treatment of **2** with $t\text{-Bu}_3\text{SiNHLi}$ in toluene yielded complex **1** as the major product.

The single bulky imido ligand in complex **2** did not significantly improve the stability of alkyl derivatives toward reduction,[14] as compared to the case for the analogous, less crowded, complexes $\text{RN{=}VCl}_3$ (R = t-Bu,[5] 4-$\text{C}_6\text{H}_4\text{Me}$,[3] 2,6-$\text{C}_6\text{H}_3\text{-Me}_2$[13]). The presence of the additional amido ligand in complex **1** resulted, by contrast, in the isolation of highly stable alkyl complexes **3** (see eq 2).

The mixed alkyl halide complexes **3a** and **3b** are pure crystalline compounds, whereas **3c** is a slightly impure waxy solid.[15] The NMR spectra of complexes **3**, which

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(9) All complexes (except **3c**) gave satisfactory elemental analyses and have also been characterized by ^{1}H, ^{13}C, and ^{51}V NMR (in C_6D_6), IR, and mass spectroscopy. Full details may be found in the supplementary material.

(10) **1**: ^{1}H NMR δ 15.8 (NH), 1.34, 1.23 (CMe_3); ^{13}C NMR δ 30.8, 30.7 ($\text{C}Me_3$), 26.0, 24.7 ($C\text{Me}_3$); ^{51}V NMR δ −65 ($\Delta\nu_{1/2}$ = 200 Hz); IR (n-pentane, ν, cm^{-1}) 3320 (NH). Anal. Calcd for $\text{C}_{24}\text{H}_{55}\text{N}_2\text{Cl}_2\text{Si}_2\text{V}$: C, 52.44; H, 10.08; N, 5.10; Cl, 12.90; Si, 10.22; V, 9.27. Found: C, 52.19; H, 10.13; N, 5.09; Cl, 12.79; Si, 9.95; V, 9.05.

(11) **2**: ^{1}H NMR δ 1.20 (CMe_3); ^{13}C NMR δ 30.6 ($\text{C}Me_3$), 26.9 ($C\text{Me}_3$); ^{51}V NMR δ 50 ($\Delta\nu_{1/2}$ = 370 Hz). Anal. Calcd for $\text{C}_{12}\text{H}_{27}\text{NCl}_3\text{SiV}$: C, 38.88; H, 7.29; N, 3.78; Cl, 28.71; Si, 7.58; V, 13.75. Found: C, 38.83; H, 7.37; N, 3.74; Cl, 28.80; Si, 7.56; V, 13.80.

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(14) Although $(t\text{-Bu}_3\text{SiN})\text{V}(\text{CH}_2\text{SiMe}_3)_3$ could be isolated as a red oil, the partially alkylated complexes $(t\text{-Bu}_3\text{SiN})\text{V}(\text{CH}_2\text{SiMe}_3)_n\text{Cl}_{3-n}$ (n = 1, 2) could be obtained only as complex product mixtures.[13]

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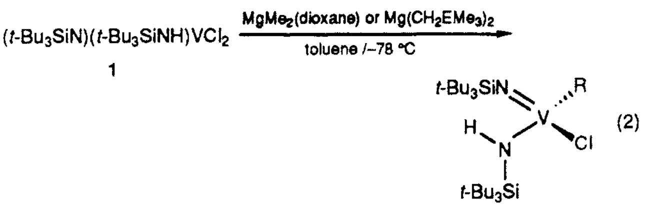

(2)

3a, R = Me
b, R = CH_2-*t*-Bu
c, R = CH_2SiMe_3

each contain a chiral center, are consistent with the presence of only one pair of enantiomers. The amido hydrogen atom is believed to lie in the same plane as the vanadium and two nitrogen atoms (to ensure maximum orbital overlap at vanadium)[16] and to point *toward* the imido group (to minimize steric crowding). The ^{13}C NMR spectra[15] of the alkyl complexes show a broad plateau-form resonance for the α-carbon of the alkyl ligand. The broadness of this resonance—$\Delta\nu_{1/2} = 400$ Hz for **3a**, for example—is caused by a combination of unresolved coupling to the $I = {}^7/_2$ vanadium nucleus and quadrupolar relaxation effects.[4a,5b] In line with the results of previous studies[3] the replacement of a chloride in **2** by an alkyl group in complexes **3** results in a distinct downfield shift change in the ^{51}V NMR spectrum.[15]

Unlike other high-oxidation-state alkylvanadium halide species,[3,17] complexes **3** are very robust; a solution of **3b** in C_6D_6, for example, is stable at high temperatures, decomposing only at 100 °C with a $t_{1/2}$ value of ca. 10 h to unidentified products. Such stability may reflect the steric unfavorability of intermolecular decomposition reactions. Nevertheless, species **3** offers the potential for forming stable derivatives by halide substitution or removal.

Reaction of complex **1** with excess LiMe in diethyl ether (eq 3) gave the new yellow crystalline product **4**, which was alternatively obtained from the reaction of **3a** with excess LiMe. The observation of equivalent imido ligands in the

$$\underset{\mathbf{1}}{(t\text{-}Bu_3SiN)(t\text{-}Bu_3SiNH)VCl_2} + 3LiMe \xrightarrow[-78\ ^\circ C]{Et_2O} \underset{\mathbf{4}}{Li[(t\text{-}Bu_3SiN)_2VMe_2]} \quad (3)$$

NMR spectrum of complex **4**[18] and the elemental analysis were consistent with formulation as the solvent-free complex Li[(*t*-$Bu_3SiN)_2VMe_2$]. The amide ligand in the putative initial product (*t*-Bu_3SiN)(*t*-$Bu_3SiNH)VMe_2$ is presumably rapidly deprotonated by LiMe. Reaction of **1** with only 2 equiv of LiMe in an attempt to form the neutral dimethyl complex gave instead a mixture of **3a** and **4**. Remarkably, the Li salt **4** is pentane-soluble, indicating close association of the Li^+ and the [(*t*-$Bu_3SiN)_2VMe_2]^-$ moieties.

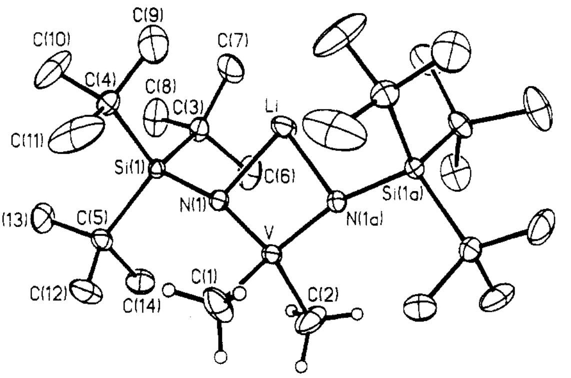

Figure 1. Molecular structure of **4**. One of the two conformations of the *tert*-butyl groups centered at C(3) and C(5) is shown in each case. Hydrogen atoms on the *tert*-butyl groups are omitted for clarity. Bond lengths (Å): V–C(1) = 2.057 (8), V–C(2) = 2.043 (5), V–N(1) = 1.705 (3), V⋯Li = 2.482 (12), Li–N(1) = 1.987 (3), N(1)–Si(1) = 1.723 (3). Bond angles (deg): C(1)–V–C(2) = 113.3 (3), C(1)–V–N(1) = 109.1 (1), C(2)–V–N(1) = 109.8 (2), N(1)–V–N(1a) = 105.5 (2), V–N(1)–Li = 84.1 (3), V–N(1)–Si(1) = 164.1 (2), Li–N(1)–Si(1) = 111.8 (3), N(1)–Li–N(1a) = 86.2 (5), N(1)–Si(1)–C(3) = 105.2 (1), N(1)–Si(1)–C(4) = 105.6 (1), N(1)–Si(1)–C(5) = 109.2 (2).

In the structure of **4**[19] (Figure 1), which has approximate C_{2v} and exact C_s symmetry, the lithium ion is bonded to the imido nitrogens rather than to the vanadium methyl groups. The methyl groups of two of the three *tert*-butyl groups are disordered, the two conformations differing by a rotation of ca. 30° about the Si–C axis, and only one of the two conformations is shown in Figure 1.

Complex **4** is the first structurally characterized alkylvanadium(V) compound, and the V–C bond distances of 2.043 (8) and 2.057 (8) Å are the shortest yet reported for a V–C single bond.[20] Coordination of lithium results in bending of the imido ligands from linearity, the V–N(1)–Si(1) angle being 164.1 (2)° compared to 177.5 (7)° in $Me_3SiN{=}VCl_3$.[21] Further, the large V–N(1) distance of 1.705 (3) Å compared to the corresponding value of 1.59 (1) Å in $Me_3SiN{=}VCl_3$[21] suggests that π-donation to vanadium from each nitrogen lone pair is reduced by coordination of lithium. The Li–N(1) distance of 1.987 (3) Å is ca. 0.1–0.2 Å less than that generally found in complexes containing a chelating diamine such as *N,N,N′,N′*-tetramethylethylenediamine.[22] Although the lithium atom is formally two-coordinate, bonding to the imido nitrogen atoms, there is also a short transannular distance of 2.482 (12) Å to vanadium; further, four short Li–H contacts of ca. 2.2–2.3 Å involving two of the methyl groups of each imido ligand effectively shield the lithium from intermo-

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(15) **3a**: ^1H NMR δ 9.2 (NH), 1.39, 1.34 (CMe_3), the VMe resonance was not observed; ^{13}C NMR (toluene-d_8, −70 °C) δ 50.5 ($\Delta\nu_{1/2} = 400$ Hz, VMe), 29.2 ($C\mathit{Me}_3$), 23.7, 22.5 ($\mathit{C}Me_3$); ^{51}V NMR δ 570 ($\Delta\nu_{1/2} = 230$ Hz); IR (*n*-hexane, ν, cm^{-1}) 3304 (NH). Anal. Calcd for $C_{25}H_{58}N_2ClSi_2V$: C, 56.73; H, 11.05; N, 5.29; Cl, 6.70; Si, 10.61; V, 9.62. Found: C, 56.95; H, 10.97; N, 5.07; Cl, 6.60; Si, 10.54; V, 9.73. **3b**: ^1H NMR δ 11.6 (NH), 3.5, 2.5 ($\Delta\nu_{1/2} = 70$ Hz, $C\mathit{H}_2CMe_3$), 1.41, 1.30 (CMe_3), 1.29 ($CH_2C\mathit{Me}_3$); ^{13}C NMR δ 101–90 ($\mathit{C}H_2CMe_3$), 38.1 ($CH_2\mathit{C}Me_3$), 34.1 ($CH_2C\mathit{Me}_3$), 31.1, 30.9 ($C\mathit{Me}_3$), 25.5, 24.4 ($\mathit{C}Me_3$); ^{51}V NMR δ 386 ($\Delta\nu_{1/2} = 180$ Hz); IR (*n*-hexane, ν, cm^{-1}) 3308 (NH). Anal. Calcd for $C_{29}H_{66}N_2ClSi_2V$: C, 59.50; H, 11.36; N, 4.79; Cl, 6.06; Si, 9.60; V, 8.70. Found: C, 59.29; H, 11.28; N, 4.62; Cl, 5.95; Si, 9.68; V, 8.69. **3c**: ^1H NMR δ 11.7 (NH), 3.8, 2.8 ($\Delta\nu_{1/2} = 70$ Hz, $C\mathit{H}_2SiMe_3$), 1.39, 1.28 (CMe_3), 0.34 ($CH_2Si\mathit{Me}_3$); ^{13}C NMR δ 83–73 ($\mathit{C}H_2SiMe_3$), 31.2 ($\mathit{C}Me_3$), 25.8, 24.4 ($C\mathit{Me}_3$), 2.8 ($CH_2Si\mathit{Me}_3$); ^{51}V NMR δ 279 ($\Delta\nu_{1/2} = 150$ Hz); IR (*n*-hexane, ν, cm^{-1}) 3311 (NH).

(16) By analogy, for example, to the structurally characterized isoelectronic (assuming π-donation occurs for both the imido and the amido ligands in **3**) complex $W(CHPh)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)$: Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

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(18) **4**: ^1H NMR δ 1.27 (CMe_3), 0.93 ($\Delta\nu_{1/2} = 35$ Hz, VMe); ^{13}C NMR (toluene-d_8, −25 °C) δ 41 ($\Delta\nu_{1/2} = 800$ Hz, VMe), 29.7 (CMe_3), 23.6 (CMe_3); ^{51}V NMR δ 417 ($\Delta\nu_{1/2} = 220$ Hz). Anal. Calcd for $C_{26}H_{60}N_2LiSi_2V$: C, 60.66; H, 11.75; N, 5.44; Li, 1.35; Si, 10.91; V, 9.89. Found (repeat analysis in brackets): C, 60.48 (61.27); H, 11.62 (11.88); N, 5.30 (5.44); Li, 1.19; Si, 11.85 (10.95); V, 10.10 (10.00).

(19) Crystal data for **4**: $C_{26}H_{60}LiN_2Si_2V$, $M_r = 514.8$, monoclinic, space group $P2_1/m$ (No. 11), $a = 8.434$ (2) Å, $b = 25.193$ (6) Å, $c = 8.702$ (2) Å, $\beta = 118.23$ (2)°, $V = 1629.1$ (6) Å^3, $Z = 2$, $D_x = 1.05$ g cm^{-3}, $F(000) = 568$ electrons, $T = 200$ K, graphite-monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 3.8 cm^{-1}; $R = 0.065$, $R_w = 0.072$, and $S = 2.24$ for 2453 independent, absorption-corrected intensities with $I > 2\sigma(I)$ and $4 < 2\theta < 50°$.

(20) (a) For comparison, the V–C distances in V(mesityl)$_4$ are in the range 2.071 (8)–2.095 (7) Å.[8b] (b) Głowiak, T.; Grobelny, R.; Jeżowska-Trzebiatowska, B.; Kreisel, G.; Seidel, W.; Uhlig, E. *J. Organomet. Chem.* **1978**, *155*, 39.

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lecular interactions. A related coordination environment for lithium has been observed in $LiAl(N{=}C\text{-}t\text{-}Bu_2)_4$[23] and in complexes containing very bulky alkoxides.[24]

The use of bulky nitrogen-based ligands has allowed the isolation of thermally stable four-coordinate alkyl complexes, which, in preliminary experiments, do not show reactivity toward olefins. Efforts are in progress to synthesize more reactive alkylvanadium complexes, a long-term goal being the formation of coordinatively and electronically unsaturated three-coordinate species.

Registry No. 1, 127971-45-3; 2, 127971-46-4; 3a, 127971-47-5; 3b, 127971-48-6; 3c, 127971-43-1; 4, 127971-44-2; $VOCl_3$, 7727-18-6; $t\text{-}Bu_3SiNHLi$, 82135-42-0.

Supplementary Material Available: Full details of the preparation and characterization of the compounds, details of the structure determination of 4, and tables of the atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen atomic parameters (11 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Selective Synthesis of Functionalized Alkylidynetriosmium Compounds via Silicon and Tin Reagents

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Summary: Selective transformation of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (**1**) to a variety of the functionalized triosmium alkylidyne cluster compounds $H_3Os_3(CO)_9(\mu_3\text{-}CR)$ (R = $CH_2CH{=}CH_2$ (**2**), H (**3**), CH_3 (**4**), Ph (**5**), $p\text{-}C_6H_4CH_3$ (**6a**), $CH_2C(O)Bu^t$ (**7**)) is achieved by the treatment of **1** with $AgSbF_6$ in the presence of silicon and tin nucleophiles. Acyl functional groups (R = C(O)OMe (**9**), $C(O)CH_2CH{=}CH_2$ (**10**), $C(O)CH_2C(O)Bu^t$ (**11**)) are also introduced by the reaction of **1** with $AgSbF_6$ under a CO atmosphere followed by the treatment with nucleophiles.

In comparison with the classic organometallic cluster chemistry of alkylidynetricobalt compounds, $Co_3(CO)_9(\mu_3\text{-}CR)$,[1] the derivative chemistry of isoelectronic iron triad alkylidyne clusters, $H_3M_3(CO)_9(\mu_3\text{-}CR)$ (M = Fe, Ru, Os),[2,3] has been much less developed. For example, the previously known purely hydrocarbyl triosmium derivatives are limited to R = H,[4,5] CH_3,[6] CH_2CH_3,[5] CH_2Ph,[7] and Ph,[8] and the procedures used are not easily generalized. However, the promoting action of Lewis acids on the formation of the halides[8-10] and the introduction of the phenyl group[8] suggest that these reactions proceed via a carbocationic intermediate. These observations prompted us to examine reactions with nucleophilic silicon and tin reagents expected to capture such a transient species.[11]

Table I. Transformation of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (1) to $H_3Os_3(CO)_9(\mu_3\text{-}CR)$

entry no.	Nu	conditions	R (product)	yield, %
1	$CH_2{=}CHCH_2\text{-}SiMe_3$	reflux, 6 h	$CH_2CH{=}CH_2$ (2)	96
2	$HSiEt_3$	room temp, 5 min	H (3)	99
3	Me_4Sn	room temp, 5 min	CH_3 (4)	85
4	Et_4Sn	room temp, 5 min	H (3)	69
5	C_6H_6	reflux, 3 h	Ph (5)	97
6	Ph_4Sn	reflux, 2 h	Ph (5)	56
7	$CH_3C_6H_5$	reflux, 3 h	$C_6H_4CH_3$ (**6a** + **6b**)[a]	83
8	$(p\text{-}CH_3C_6H_4)_4Sn$	reflux, 2 h	$p\text{-}C_6H_4CH_3$ (**6a**)	51
9	$CH_2{=}C(Bu^t)\text{-}OSiMe_3$	room temp, 12 h	$CH_2C(O)Bu^t$ (7)	55
10	(1) CO + (2) MeOH	room temp, 10 min[b]	C(O)OMe (9)	45
11	(1) CO + (2) $CH_2{=}CHCH_2\text{-}SiMe_3$	reflux, 1 h[b]	$C(O)CH_2CH{=}CH_2$ (10)	25
12	(1) CO + (2) $CH_2{=}C(Bu^t)\text{-}OSiMe_3$	reflux, 3 h[b]	$C(O)CH_2C(O)Bu^t$ (11)[c]	34
13	(1) CO + (2) $HSiEt_3$	reflux, 6 h[b]	CH_3 (4)	61

[a] **6a**:**6b** = 2.2:1. [b] Conditions for step 2. [c] A 10:1 mixture of the enol and keto tautomers (see text).

When $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (**1**)[9] was treated with excess $AgSbF_6$ in refluxing CH_2Cl_2 in the presence of allyltrimethylsilane, the anticipated product $H_3Os_3(CO)_9(\mu_3\text{-}CCH_2CH{=}CH_2)$ (**2**)[12] was obtained in almost quantitative yield (eq 1). Analogous reactions led to other new prod-

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[12] A typical procedure is as follows. A CH_2Cl_2 solution (4 mL) of $AgSbF_6$ (274 mg, 0.80 mmol) was added to a mixture of **1** (70.0 mg, 0.0762 mmol) and $CH_2{=}CHCH_2SiMe_3$ (0.5 mL) dissolved in 2 mL of CH_2Cl_2, and the mixture was refluxed for 6 h. After the consumption of **1** was checked by TLC, the volatiles were removed under reduced pressure. Extraction with ether, filtration through silica gel, and preparative TLC separation (silica gel; CH_2Cl_2/hexane, 1:3) gave **2** (64.5 mg, 0.0735 mmol; 96%). The amounts of $AgSbF_6$ and allylsilane were not optimized. **2**: ^1H NMR ($CDCl_3$) δ 6.24 (1 H, ddt, J = 17.7, 9.8, 7.4 Hz, ═CH–), 5.21 (1 H, dd, J = 17.7, 2.0 Hz, ═CH_2, trans), 5.05 (1 H, dd, J = 9.8, 2.0 Hz, ═CH_2, cis), 4.82 (2 H, d, J = 7.4 Hz, CH_2), −18.86 (3 H, s, Os—H); IR (C_6H_{12}) 2077 (vs), 2018 (vs), 2006 (m) cm^{-1}. Anal. Calcd for $C_{13}H_8O_9Os_3$: C, 17.77; H, 0.92. Found: C, 17.91; H, 0.85.

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